telomerization investigations reviewed in this Account. VIK acids are of considerable commercial interest. Their industrial applications depend strongly on structure of initial acids, number and structure of substituents present, and length of main chains. Three types of acids are obtained on an industrial scale: C_{5-9}, C_{11-19}, and $C_{>19}$. VIK are used in the production of

(46) R. Kh. Freidlina, A. B. Terent'ev, Yu. P. Chizhov, N. S. Ikonnikov, French Patent 1,537,490 (1967); *Chem. Abstr.*, 71, 101319g (1969).

oil-free coatings—lacquers and enamels for cars and household machinery—having good decorative and protective properties.[47]   VIK have also found applications as extractants for isolation and separation of nonferrous and rare metals from aqueous solutions of their salts.[48]

(47) R. Kh. Freidlina, A. B. Terent'ev, P. M. Bogatyrev et al., French Patent 2,091,907 (1974); *Chem. Abstr.*, 83, 81407b (1975).
(48) A. V. Nikolaev, A. I. Khol'kin, R. Kh. Freidlina, A. B. Terent'ev et al., *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 52 (1972).

Catalysis by Alloys and Bimetallic Clusters

John H. Sinfelt

Corporate Research Laboratories, Exxon Research and Engineering Co., Linden, New Jersey

Bimetallic catalysts have been of interest for investigating the so-called "electronic factor" in catalysis by metals.[1-6]   Transition metals, especially the metals of group 8, are the active catalysts for many reactions.[7] In terms of the electron-band theory, a group 8 metal such as nickel is characterized as having an incompletely filled d band, whereas a group 1B metal such as copper has a filled d band. According to the original view of Mott and Jones,[8] an alloy of a group 8 metal with a group 1B metal is characterized by a d band which is filled to a greater extent than that of the pure group 8 metal. In the case of a nickel–copper alloy, the substitution of copper atoms for nickel atoms in the metal lattice adds extra electrons to the lattice. The extra electrons introduced with the copper enter the d band until it is filled. By varying the composition of the alloy, one can alter the degree of filling of the d band with electrons and observe the effect on catalytic activity.

In the model of electronic structure just described for the alloys, which is known as the "rigid band" model, there is a single d band for the alloy as a whole, with no differentiation between the different types of atoms in the alloy with regard to their chemical bonding properties. This model of the electronic structure of group 8–group 1B metal alloys has been challenged in recent years.[9-12]   According to the more recent view, there are separate d bands characteristic of each component of the alloy. In any case, the experimental data on chemisorption and catalysis indicate that the different types of atoms in the surface of the alloy, e.g., nickel and copper, retain their chemical differences, although bonding properties of the atoms are probably altered to some degree.[13]   Present efforts to elucidate the electronic factor in catalysis by alloys are proceeding

from this point of view, which resembles the idea of "ligand" effects in the chemistry of organometallic complexes.[14]

Although progress in the use of alloys to elucidate the electronic factor in metal catalysis has been slow, interest in bimetallic systems has not declined. In fact, there has been a great revival of interest in the field in recent years, for reasons other than a renewed probing into the electronic factor alone. These include (a) the realization that bimetallic systems may exhibit major selectivity effects in catalysis, i.e., markedly different behavior toward different types of reactions,[15-20] and (b) the development of the idea of highly dispersed bimetallic systems, i.e., "bimetallic cluster" catalysts.[17,21]

The selectivity features of bimetallic catalysts have only recently received any attention. Early studies of the electronic factor emphasized the relation between alloy composition and catalytic activity for hydrogenation reactions in which selectivity was not a consideration. Typical reactions investigated were the hydrogenation of benzene to cyclohexane[4] and ethylene to ethane.[5,6] It has now been shown that the addition of a group 1B metal to a group 8 metal decreases

(1) G. M. Schwab, *Discuss. Faraday Soc.*, 8, 166 (1950).
(2) D. A. Dowden, *J. Chem. Soc.*, 242 (1950).
(3) D. A. Dowden and P. Reynolds, *Discuss. Faraday Soc.*, 8, 184 (1950).
(4) W. K. Hall and P. H. Emmett, *J. Phys. Chem.*, 62, 816 (1958).
(5) W. K. Hall and P. H. Emmett, *J. Phys. Chem.*, 63, 1102 (1959).
(6) R. J. Best and W. W. Russell, *J. Am. Chem. Soc.*, 76, 838 (1954).
(7) J. H. Sinfelt, *Progr. Solid-State Chem.*, 10 (2), 55 (1975).
(8) N. F. Mott and H. Jones, "Theories of the Properties of Metals and Alloys", Oxford University Press, London, 1936.
(9) D. H. Seib and W. E. Spicer, *Phys. Rev. Lett.*, 20, 1441 (1968).
(10) C. D. Gelatt and H. Ehrenreich, *Phys. Rev. B*, 10, 398 (1974).
(11) P. Soven, *Phys. Rev.*, 156, 809 (1967).
(12) B. Velicky, S. Kirkpatrick, and H. Ehrenreich, *Phys. Rev.*, 175, 747 (1968).
(13) W. M. H. Sachtler and P. van der Plank, *Surf. Sci.*, 18, 62 (1969).
(14) W. M. Sachtler, *LeVide*, 164, 67 (1973).
(15) J. H. Sinfelt, J. L. Carter, and D. J. C. Yates, *J. Catal.*, 24, 283 (1972).
(16) J. H. Sinfelt, A. E. Barnett, and J. L. Carter, U.S. Patent 3,617,518 (1971).
(17) J. H. Sinfelt, *J. Catal.*, 29, 308 (1973).
(18) J. H. Sinfelt, Y. L. Lam, J. A. Cusumano, and A. E. Barnett, *J. Catal.*, 42, 227 (1976).
(19) V. Ponec and W. M. H. Sachtler, *J. Catal.*, 24, 250 (1972).
(20) J. M. Beelen, V. Ponec, and W. M. H. Sachtler, *J. Catal.*, 28, 376 (1973).
(21) J. H. Sinfelt, *Chem. Eng. News*, 50, 18 (July 3, 1972).

markedly the activity of the latter for the rupture of carbon–carbon bonds in hydrogenolysis reactions of hydrocarbons, but has a much smaller effect on other hydrocarbon reactions such as hydrogenation and dehydrogenation.[15–18] While an electronic factor would in general be expected to influence the selectivity as well as the activity of bimetallic catalysts, the recent work indicates that purely geometric factors at a surface may play a crucial role in determining selectivity. If one reaction requires a surface site consisting of a number of adjacent active metal atoms, while another requires a site consisting of only one active metal atom, the former will be more sensitive than the latter to inclusion of inactive foreign metal atoms in the surface. Furthermore, in systems of a group 8 metal and a group 1B metal, the latter may concentrate strongly in the surface, so that its influence may be dramatic even at very low concentrations. In general, the surface composition of a bimetallic catalyst cannot be assumed to be identical with the bulk composition, as recent work in this field has clearly shown.[13–15]

For a bimetallic catalyst to be of interest for industrial applications, it is necessary that it be prepared in a high surface area form and that it be resistant to loss of surface area during use. Dispersing it on a carrier provides an effective approach to the problem. The resulting catalyst is called a "bimetallic cluster" rather than an alloy, since systems of interest include metallic combinations which do not form alloys in the bulk.[17,21] The more general term "polymetallic cluster" is used in referring to any cluster composed of atoms of two or more metals, and hence includes a "bimetallic cluster" as a special case. The dispersion, defined as the fraction of the atoms in a cluster which are present in the surface, depends on the system and conditions of preparation. In some cases the dispersion approaches unity. The clusters are then extremely small, of the order of 10 Å in size, or perhaps possess a two-dimensional character. Research in our laboratory on systems of this type has culminated in the development of a new reforming catalyst[21,22] which has been applied extensively in commercial operations. The reforming process is important for the production of high antiknock quality motor gasolines from petroleum naphthas.[23,24]

Surface Composition of Bimetallic Catalysts

Evidence that surface and bulk compositions are different in the case of nickel–copper alloys has recently been obtained from hydrogen chemisorption studies,[15,25,26] and is based on the observation that strong chemisorption of hydrogen does not occur on copper. The addition of only a few percent of copper to nickel decreases the amount of strongly chemisorbed hydrogen severalfold, which suggests that the concentration of copper in the surface is much greater than in the bulk. The strongly chemisorbed hydrogen refers to the amount which remains on the surface after evacuation at room temperature. The data in Figure 1 suggest that copper is the predominant component in the surface of nickel–copper alloys containing as little as 5 atom %
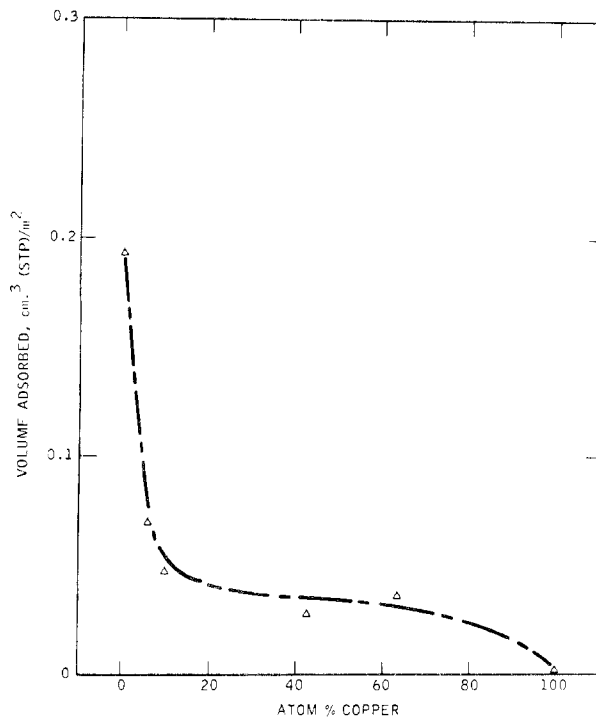
(22) R. R. Cecil, W. S. Kmak, J. H. Sinfelt, and L. W. Chambers, *Proc., Div. Refin., Am. Pet. Inst.*, **52**, 203 (1972).
(23) J. H. Sinfelt, *Adv. Chem. Eng.*, **5**, 37 (1964).
(24) J. H. Sinfelt, *Annu. Rev. Mater. Sci.*, **2**, 641 (1972).
(25) P. van der Plank and W. M. H. Sachtler, *J. Catal.*, **7**, 300 (1967).
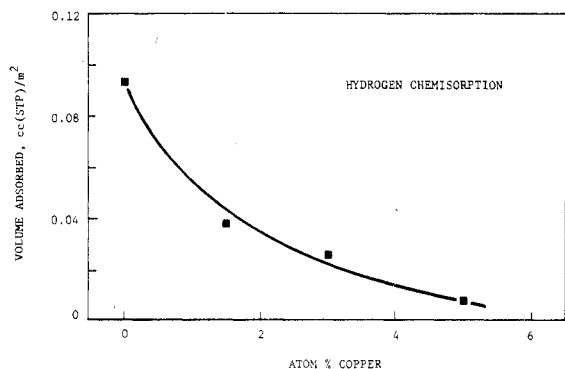(26) D. A. Cadenhead and N. J. Wagner, *J. Phys. Chem.*, **72**, 2775 (1968).

Figure 1. The chemisorption of hydrogen on copper–nickel catalysts at room temperature as a function of composition. The chemisorbed hydrogen refers to the amount that is retained on the surface after 10-min evacuation at room temperature following completion of an adsorption isotherm.[15,35]

copper. The surface areas of the catalysts in Figure 1 are of the order of 1 m^2/g (approximately one metal atom out of a thousand is a surface atom).

In the nickel–copper alloys just considered, the two components were completely miscible, since the alloys were equilibrated at a sufficiently high temperature in their preparation, i.e., 450 °C. If the nickel–copper system is equilibrated at a lower temperature, say 200 °C, there is evidence of a miscibility gap.[25] For compositions within the gap, the system consists of two phases of constant composition in equilibrium, the relative amounts of the phases depending on the overall composition. The individual phases do not exist as separate particles, but instead the copper-rich phase forms a surface layer around the nickel-rich phase.[25] A more extreme example of this type of behavior is the ruthenium–copper system, the components of which are essentially completely immiscible in the bulk. The crystal structures of the two metals are different, ruthenium having a hexagonal-close-packed structure and copper a face-centered-cubic structure. While the two components are immiscible in the bulk, there is evidence of definite interaction between the two at a surface.[17,18] Ruthenium–copper samples prepared by precipitation from aqueous solutions of salts of the metals, followed by treatment in hydrogen at elevated temperatures, consist of bimetallic aggregates in which copper tends to cover the surface of the ruthenium. Evidence for this is provided by hydrogen chemisorption data,[18] as shown in Figure 2. In the catalysts of Figure 2 approximately one metal atom out of a hundred is a surface atom. The presence of copper results in a marked decrease in the extent of hydrogen chemisorption on ruthenium, of the order of tenfold for a copper content of 5 atom %. For the ruthenium–

Figure 2. Hydrogen chemisorption on ruthenium–copper catalysts as a function of copper content. The chemisorption data were obtained at room temperature and represent the strongly chemisorbed fraction, determined as in Figure 1.[18]
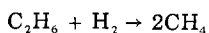
copper aggregates in Figure 2, monolayer coverage by copper would occur at a copper content of about 1.5 atom % if all the copper existed as a single layer at the surface. The data suggest that a ruthenium–copper aggregate consists of small patches or clusters of copper on the surface of a crystallite composed essentially of pure ruthenium. In agreement with this picture, x-ray diffraction patterns exhibit lines for ruthenium but not for copper. The interaction between the two components is considered analogous to that which would exist in the chemisorption of copper on ruthenium.

In bimetallic systems the component with the lower heat of sublimation often accumulates in the surface. In the case of group 8–group 1B metal combinations, this component is the group 1B metal. However, in the presence of a gas which interacts sufficiently strongly and selectively with the group 8 metal, the group 1B metal will not be the predominant component in the surface. Thus, in an oxygen atmosphere the surface of the nickel–gold system becomes rich in nickel rather than in gold.[27] Similarly, in an atmosphere of carbon monoxide the surface of palladium–silver alloys becomes enriched with palladium, whereas normally silver would be the predominant surface component.[28]

In addition to selective chemisorption methods, one may employ a variety of other methods to obtain information on the surface compositions of alloys. These include work function measurements,[29] Auger spectroscopy,[27,30] and photoelectron spectroscopy.[31] All of the methods at present have limitations from the viewpoint of obtaining precise quantitative information on surface composition, but can surely be regarded reliable for yielding qualitative or semiquantitative information.

Selectivity of Bimetallic Catalysts

A striking example of catalytic specificity is provided by recent work on nickel–copper alloy catalysts in which two different reactions were investigated, the hydrogenolysis of ethane to methane and the dehydrogenation of cyclohexane to benzene:[15]

$$C_2H_6 + H_2 \rightarrow 2CH_4$$

$$C_6H_{12} \rightarrow C_6H_6 + 3H_2$$

Figure 3. Activities of copper–nickel alloy catalysts for the hydrogenolysis of ethane to methane and the dehydrogenation of cyclohexane to benzene. The activities refer to reaction rates at 316 °C. Ethane hydrogenolysis activities were obtained at ethane and hydrogen pressures of 0.030 and 0.20 atm, respectively. Cyclohexane dehydrogenation activities were obtained at cyclohexane and hydrogen pressures of 0.17 and 0.83 atm, respectively.[15]

The effect of adding copper to nickel is markedly different for the two reactions, as shown by the data on specific activities of a series of nickel–copper alloys in Figure 3. In the case of ethane hydrogenolysis, addition of as little as 5 atom % copper to the nickel decreases catalytic activity by three orders of magnitude. Further addition of copper continues to decrease the activity. However, for cyclohexane dehydrogenation the initial increments of copper actually increase the catalytic activity of nickel. As the copper content of the alloy is increased beyond a few percent, the dehydrogenation activity is not affected much over a broad range of composition, exhibiting a marked decline only as the composition approaches pure copper.

In the hydrogenolysis of ethane on metals, it has been concluded that the ethane is chemisorbed with rupture of carbon–hydrogen bonds to form a hydrogen-deficient dicarbon surface residue, C_2H_x, which then undergoes rupture of the carbon–carbon bond to form monocarbon fragments on the surface:[32-35]

$$C_2H_6 \rightleftharpoons C_2H_x(ads) + aH_2$$

$$C_2H_x(ads) \rightarrow adsorbed\ C_1\ fragments$$

The adsorbed monocarbon fragments are then hydrogenated to methane. The symbol ads refers to adsorbed species and the quantity a is equal to $(6 - x)/2$. It is visualized that both carbon atoms in the adsorbed intermediate C_2H_x form bonds with surface metal atoms, and that more than one surface metal

(27) F. L. Williams and M. Boudart, *J. Catal.*, **30**, 438 (1973).
(28) R. Bouwman, G. J. M. Lippits, and W. M. H. Sachtler, *J. Catal.*, **25**, 350 (1972).
(29) W. M. H. Sachtler and G. J. H. Dorgelo, *J. Catal.*, **4**, 654 (1965).
(30) C. R. Helms, *J. Catal.*, **36**, 114 (1975).
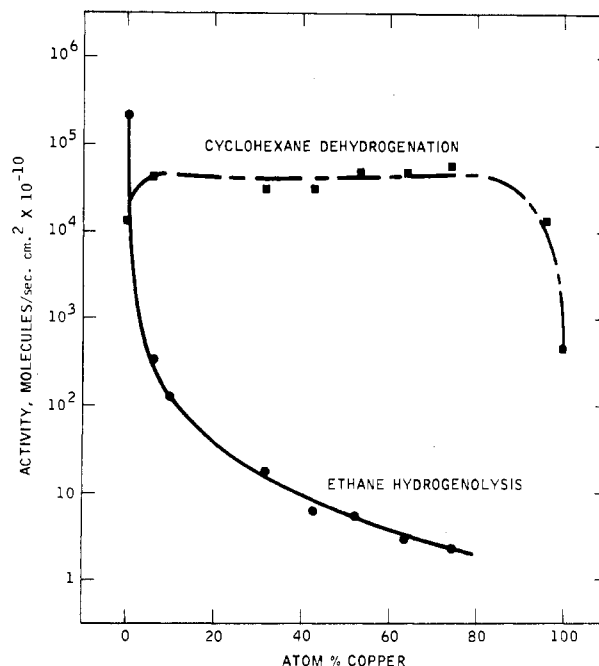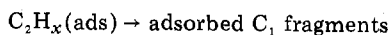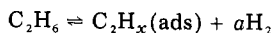(31) R. L. Park and J. E. Houston, *J. Vac. Sci. Technol.*, **10**, 176 (1973).

(32) A. Cimino, M. Boudart, and H. S. Taylor, *J. Phys. Chem.*, **58**, 796 (1954).
(33) J. H. Sinfelt, *J. Catal.*, **27**, 468 (1972).
(34) J. H. Sinfelt, *Adv. Catal.*, **23**, 91 (1973).
(35) J. H. Sinfelt, *Catal. Rev.-Sci. Eng.*, **9**, 147 (1974).

atom is involved in the bonding.

In a bimetallic combination of an inactive metal with a highly active metal, we may consider the possibility that the hydrogenolysis activity of the catalyst is dependent on the existence of sites comprising "multiplets" of active metal atoms (i.e., sites consisting of groups of adjacent active metal atoms). The term multiplet is taken from the work of Balandin.[36] The term "ensemble" has been adopted by others[19,37] in this context. As the required number of active metal atoms in a multiplet increases, the multiplet concentration becomes more sensitive to dilution of the surface with inactive metal atoms. If the latter concentrate markedly in the surface, as in the case of nickel–copper alloys, the presence of only a few percent in the alloy may decrease catalytic activity manyfold. According to this view, the only function of the surface copper atoms in nickel–copper catalysts is to dilute the nickel atoms and thus limit the number of multiplet nickel atom sites.

While such a geometric interpretation is a very reasonable one and can account for a large inhibiting effect of copper on the hydrogenolysis activity of nickel, it is difficult to dismiss the possibility that electronic interaction between copper and nickel atoms may affect the catalysis. Such an interaction has been called a "ligand" effect by Sachtler.[14,38] In view of the low ability of copper relative to nickel to chemisorb hydrocarbons, the presence of copper could decrease the strength of adsorption of hydrocarbon species. In ethane hydrogenolysis, the strength of bonding between the two carbon atoms in the chemisorbed intermediate might be expected to vary in an inverse manner with the strength of bonding of the carbon atoms to the metal. One would then conclude that rupture of the carbon–carbon bond would be inhibited by a decrease in the strength of adsorption accompanying addition of copper to nickel. If carbon–carbon rupture is rate limiting, the rate of hydrogenolysis should then decrease.

The markedly different effect of copper on the catalytic activity of nickel for cyclohexane dehydrogenation, as compared to ethane hydrogenolysis, is rationalized as follows. There is the possibility that the reaction does not require a site consisting of a multiplet of active nickel atoms, and is therefore much less sensitive to the presence of copper atoms in the surface than a reaction requiring such multiplets. While this possibility can account for the absence of a sharp decline in activity as copper is added to nickel, it does not explain why copper-rich alloys have dehydrogenation activities as high as or higher than that of pure nickel. If addition of copper to nickel decreases the strength of adsorption of hydrocarbons, and the rate-determining step is desorption of the benzene product, the activity of a catalytic site would increase and compensate for a decrease in the number of such sites. However, it is not necessary that desorption of the product be rate limiting. It is required only that the rate-determining step be one which is adversely affected by an increase in the strength of adsorption. The range of composition over which the rate is essentially constant may be
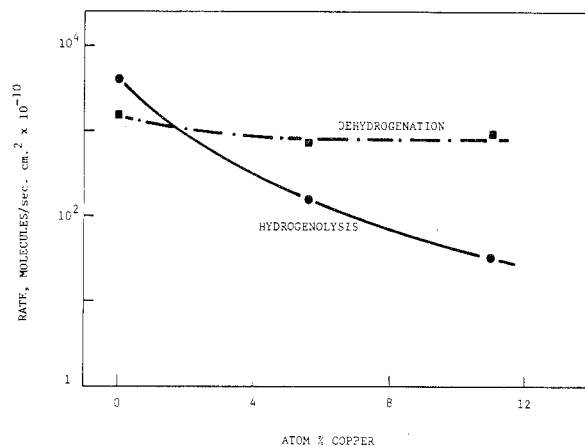
(36) A. A. Balandin, *Adv. Catal.*, 10, 96 (1958).
(37) D. A. Dowden, *Proc. Int. Congr. Catal., 5th, 1972,* 621 (1973).
(38) Y. Soma-Noto and W. M. H. Sachtler, *J. Catal.*, 32, 315 (1974).

Figure 4. The rates of dehydrogenation and hydrogenolysis of cyclohexane on ruthenium–copper catalysts as a function of composition. The rates are shown for a temperature of 316 °C and for cyclohexane and hydrogen pressures of 0.17 and 0.83 atm, respectively.[18]

characterized by relatively small variations in surface composition and heat of adsorption of the hydrocarbon. Over the range of composition from pure nickel to pure copper, it is likely that the rate-determining step changes. For pure copper, the chemisorption of the cyclohexane itself may be limiting.

Another example of a selectivity effect is provided by data on cyclohexane conversion on ruthenium–copper catalysts.[18] In cyclohexane conversion, ruthenium differs from nickel in exhibiting extensive hydrogenolysis to lower carbon number alkanes along with the dehydrogenation to benzene. Consequently, the effect of copper on the selectivity of ruthenium can be observed with a single reactant. The product of the cyclohexane hydrogenolysis reaction is predominantly methane, even at very low conversions. The presence of copper, which concentrates at the surface of the ruthenium, decreases the hydrogenolysis activity sharply. However, the effect on dehydrogenation activity is much smaller, as shown in Figure 4. This improves markedly the selectivity of conversion of cyclohexane to benzene. It seems probable that different chemisorbed intermediates are involved in the dehydrogenation and hydrogenolysis reactions. As in the case of ethane, the intermediate involved in cyclohexane hydrogenolysis is probably a hydrogen-deficient surface residue which forms bonds with more than one surface metal atom.

The hydrogenolysis activity of a ruthenium–copper catalyst is strikingly related to its capacity for strong hydrogen chemisorption, as shown by the data in Figure 5 for a number of ruthenium–copper catalysts of varied composition.[18] In ethane hydrogenolysis, it has been concluded that rupture of the carbon–carbon bond is facilitated by strong binding of the intermediate to the surface. Since it is reasonable for strong hydrocarbon chemisorption to correlate with strong hydrogen chemisorption, the relation between hydrogenolysis activity and strong hydrogen chemisorption is understandable. The exponential nature of the relation is a clear indication that ethane hydrogenolysis activity is much more sensitive to variations in the ruthenium–copper catalysts than is the capacity for strong hydrogen chemisorption. As one might expect, the selectivities of these catalysts for dehydrogenation of
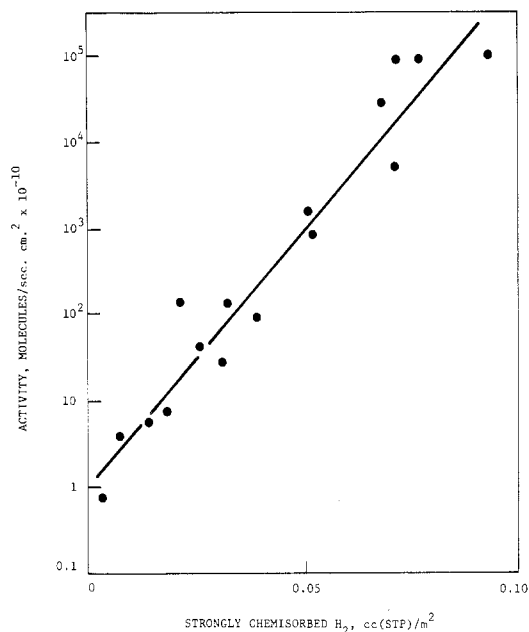
Figure 5. Correlation of ethane hydrogenolysis activity and amount of strongly chemisorbed hydrogen for ruthenium–copper catalysts. The ethane hydrogenolysis activities are rates at 245 °C and ethane and hydrogen pressures of 0.030 and 0.20 atm, respectively. The amount of strongly chemisorbed hydrogen at room temperature was determined as in Figures 1 and 2.[18]
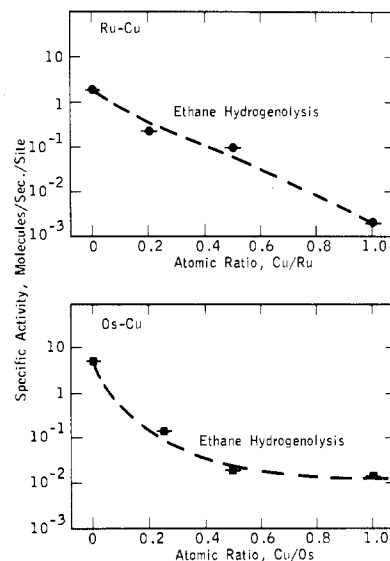

Figure 6. The specific activities of silica-supported ruthenium–copper and osmium–copper catalysts for ethane hydrogenolysis. The activities are compared at 245 °C and ethane and hydrogen pressures of 0.030 and 0.20 atm, respectively. The catalysts all contain 1 wt % of either ruthenium or osmium and varying amounts of copper.[17,35]

cyclohexane to benzene correlate inversely with strong hydrogen chemisorption.

In general, the addition of a group 1B metal to a group 8 metal has been observed to decrease hydrogenolysis activity markedly but to have a much smaller effect on such other reactions as dehydrogenation, hydrogenation, and isomerization of hydrocarbons.[15-20,39] Selectivity is clearly an important aspect of hydrocarbon catalysis by alloys.

"Bimetallic Cluster" Catalysts

A supported bimetallic catalyst can be prepared simply by wetting a suitable carrier such as silica with an aqueous solution of salts of the two metals of interest. The material is then dried and contacted with a stream of hydrogen at a temperature high enough to accomplish reduction of the metal precursors to the metallic state. This procedure results in the formation of very small metal clusters dispersed on the surface of the carrier. The nature of these metallic entities is the question of interest. Will the individual clusters be monometallic or will there be mixing of atoms of the different metals in the form of bimetallic clusters? One might expect on purely statistical grounds that the individual clusters would contain atoms of both metals. This expectation is supported by experiment, even for cases in which the individual metal components exhibit very low miscibility in the bulk.[17,40] Examples of interesting systems involving components of extremely limited miscibility are ruthenium–copper and osmium–copper supported on silica. Catalysts containing 1 wt % of either ruthenium or osmium and varying amounts of copper have been investigated.[17] The atomic ratio of copper to the group 8 metal ranged from

0 to 1. The degree of metal dispersion was high in all of these catalysts, as evidenced by the fact that x-ray diffraction scans showed no lines due to the metals. By contrast, a sample containing 1 wt % copper alone on silica gave diffraction lines characteristic of metallic copper with a crystallite size of 200 Å. The absence of lines due to copper in the case of the ruthenium–copper and osmium–copper catalysts indicates that the ruthenium and osmium interact with the copper, with the result that large copper crystallites are not formed. The observations are consistent with the existence of ruthenium–copper and osmium–copper clusters on the surface of the carrier.

Direct experimental verification of the bimetallic cluster concept is complicated by limitations in the ability of physical methods to obtain structural information on highly dispersed systems. In such a system, however, a catalytic reaction can serve as a sensitive probe to obtain evidence of interaction between the atoms of the two metallic components. For supported bimetallic combinations of a group 8 and a group 1B metal, the hydrogenolysis of ethane to methane is a very useful reaction for this purpose. In applying ethane hydrogenolysis as a probe to establish interaction between copper and either ruthenium or osmium on a carrier, one simply looks for a marked suppression of hydrogenolysis activity of the group 8 metal when copper is present.

Data on hydrogenolysis activities of the ruthenium–copper and osmium–copper catalysts described in the previous paragraphs are shown in Figure 6. A measure of the number of surface sites in each catalyst is provided by data on the chemisorption of hydrogen at room temperature, each surface site corresponding to one atom of adsorbed hydrogen. This makes it possible to determine specific activity, i.e., the catalytic activity per surface site. Such a definition of specific activity is useful for normalizing the catalytic activity data, but should not be interpreted to mean that a hydrocarbon molecule undergoing reaction requires only

(39) V. Ponec and W. M. H. Sachtler, *Proc. Int. Congr. Catal., 5th, 1972*, 645 (1973).

(40) J. H. Sinfelt, *Proc. Int. Congr. Catal., 5th, 1972*, 653 (1973).
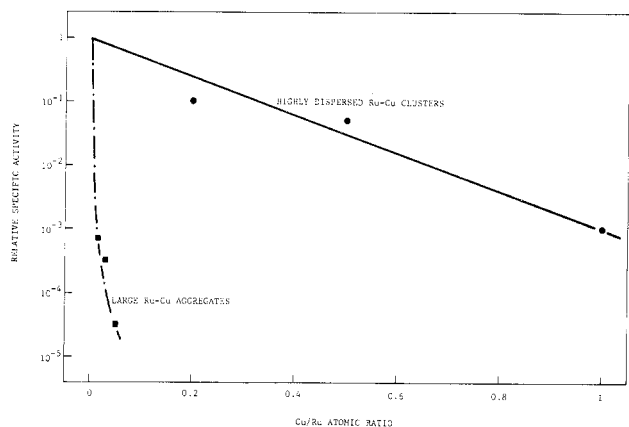
Figure 7. Influence of the state of dispersion of ruthenium–copper catalysts on the relationship between ethane hydrogenolysis activity and catalyst composition. The large ruthenium–copper aggregates have a metal dispersion of the order of 1%, while the highly dispersed ruthenium–copper clusters have a metal dispersion of the order of 50%.[18]

a simple surface site of the type defined by the hydrogen chemisorption data. The data of Figure 6 provide strong evidence of interaction between copper and the group 8 metal, and thus support the bimetallic cluster concept. Since incorporation of copper with the group 8 metal decreases the hydrogenolysis activity markedly, the metal components are clearly not isolated from each other on the carrier.

It is of interest to consider how the state of dispersion of ruthenium–copper catalysts affects the relationship between ethane hydrogenolysis activity and catalyst composition.[18] A comparison of large ruthenium–copper aggregates with highly dispersed ruthenium–copper clusters is given in Figure 7. The dispersion, defined as the percentage of metal atoms present in the surface, is of the order of 1% for the large ruthenium–copper aggregates and of the order of 50% for the ruthenium–copper clusters. The presence of one atom of copper per atom of ruthenium decreases the hydrogenolysis activity of ruthenium by 1000-fold in the case of the highly dispersed clusters. The same inhibiting effect of the copper is found with the large ruthenium–copper aggregates when the amount of copper is only 1–2% of the amount of ruthenium in the catalyst. A similar conclusion is reached when hydrogen chemisorption data on these systems are compared.[18] Clearly, the highly dispersed ruthenium–copper clusters require a much higher atomic ratio of copper to ruthenium than the large ruthenium–copper aggregates

to achieve a given inhibiting effect. The required ratios differ by a factor approximately equal to the ratio of the metal dispersions of the catalysts. This indicates that the copper in a ruthenium–copper aggregate is confined to the surface, which is consistent with the extremely low miscibility of the two metals in the bulk state. If one envisions a series of ruthenium–copper aggregates of varying size, each comprising a monolayer of copper on a ruthenium core, the atomic ratio of copper to ruthenium in an aggregate will increase with decreasing aggregate size. From this simple consideration, it is readily seen how a highly dispersed bimetallic cluster may have compositions far outside the range of those possible in a bulk solid solution of the two metals.

As a result of their low hydrogenolysis activities, bimetallic clusters of a group 8 and a group 1B metal are more selective than the pure group 8 metal for a reaction such as the conversion of cyclohexanes to aromatics.[17] However, they are not the only types of bimetallic clusters of interest. Others include combinations of two group 8 metals, e.g., platinum–palladium, platinum–rhodium, and platinum–iridium.[41]

Our present knowledge of "bimetallic clusters" is derived largely from studies of their chemisorption and catalytic properties. However, in the case of platinum–iridium catalysts, x-ray diffraction has proved to be very useful in providing direct evidence for the existence of platinum–iridium clusters in the approximate size range of 25–50 Å.[41] As already pointed out, it becomes increasingly difficult to characterize such systems by conventional physical methods as the degree of metal dispersion increases. In recent years, there have been advances in the area of x-ray absorption spectroscopy which hold much promise for this purpose. It has been shown that analysis of extended x-ray absorption fine structure (EXAFS) can yield structural information on highly dispersed, noncrystalline materials.[42] The application of EXAFS to bimetallic catalysts is currently being investigated by the author and his collaborators.[43]

(41) J. H. Sinfelt, U.S. Patent 3,953,368 (1976).

(42) D. E. Sayers, F. W. Lytle, and E. A. Stern, *Phys. Rev. Lett.*, **27**, 1204 (1971).

(43) F. W. Lytle, G. H. Via, and J. H. Sinfelt, *Prepr., Div. Pet. Chem., Am. Chem. Soc.*, **21** (2), 366 (1976).